THE USE OF CARBON FIBER COMPOSITES AS SUBSTRATE FOR A ZERO VALENT METAL DECHLORINATION SYSTEM.

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Abstract

The use of zero valent metals is known to successfully degrade chlorinated hydrocarbons.
The use of zinc metal to decholorinate trichloroethene (TCE) in contaminated groundwater sources
has been limited by metal surface area for reaction. A highly porous carbon fiber composite substrate
for the zinc metal provides a much higher surface area for reaction in a decholorination system. The
zinc coating applied to the carbonaceous fibers provides higher reaction rates than traditional
powdered metal systems. Added advantages of using the zinc coated carbon substrate for ground
water clean up are low pressure drop, easy removal and emplacement of composites, and the ability
to recharge the zinc coating *in situ*. The novel zinc impregnation method results in a uniform coating
of zinc throughout the composite and a greatly increased area for reaction.

Introduction

The dehalogenation of hydrocarbons by zero-valent metals offers many attractive features for
environmental application. The relatively high reaction rates, low cost of the metal catalyst, and
non-contaminating nature of the catalyst all make this an attractive system for ground water clean-
up. The limiting factor for the dehalogenation reaction is the surface area of the metal available for
reaction. Large metal pellets offer slow reaction rates, while fine metal particles lead to faster
reaction rates. In this study, a carbon fiber composite is used as a support for zinc plating; producing
a supported zinc catalyst with very high surface area for reaction and low resistance to flow. The
zinc plated composite system also has the advantage of being regenerable after metal depletion. This
regeneration could be performed *in situ*.

The decholorination of trichloroethene (TCE) by zero-valent zinc is demonstrated with both
supported and unsupported zinc systems. Initial rate constants for this reaction are reported. The zinc
was placed onto the carbon composite using electrochemical reaction at low current densities and the
resistance to flow through the composite was measured and compared to uncoated composite.

Literature Review

The use of zero-valent metals, mainly iron, tin and zinc, to remediate water containing
chlorinated hydrocarbons has been proposed by several researches. The emphasis of most research in
this area has been on the use of iron as the metallic catalyst or a modified iron, such as the palladium
plated iron granules used by Korte et. al. (1-7) Boronina et. al. (8) have demonstrated the efficacy of
using Zn or Sn as the catalytic metal, showing the relatively fast reaction rates obtained using very
fine Zn particles in an inert atmosphere.

The destruction of chlorinated species into metal salts and dechlorinated byproducts has been
shown to occur at reaction rates ranging from 5 to 15 orders of magnitude faster than that observed
for natural abiotic processes. (6) O'Hannesin et. al. have shown that a reactive bed containing Fe
filings was able to remove 90% of the trichloroethene (TCE) from groundwater at the Canadian
Forces Base, Borden, Ontario site. They concluded that the reaction rate was independent of TCE
concentration . In further studies, this group found chlorinated species destruction by granular iron of
13 out of 14 halogenated methanes, ethanes and ethenes. (6)

In building a pilot scale operation for the reduction of TCE using iron filings, MacKenzie et.
al. (7) determined several factors controlling the process. The alkalinity of the ground water being ·
treated as well as the amount of dissolved oxygen in the water effect catalytic bed lifetime. The
presence of carbonate or oxide forming species in the water leads to a inert layer of metal oxide or
metal carbonate forming on the metal surface. This layer greatly reduces the overall reaction rate.
(1,5,7,8). MacKenzie et. al. found that a 10 fold increase in aqueous alkalinity reduced the reaction
rate by three fold.

Metallic surface area is a controlling factor in the rate of reaction. (1, 8) Boronina et.al. (8)
have shown that cryo-particle Zn with a surface area of >65 m^2/g reduced the concentration of CCl$_4$
in water by over 90% in three hours, while granular Zn, having a surface area < 1 m^2/g, achieved a

reduction of only 25%. A similar correlation between surface area and dechlorinating ability was seen in studies using Sn metal.

Objectives

This paper describes a novel process for supporting zero-valent zinc on a carbon fiber composite. The study also reports some preliminary rate constants for unsupported and supported zinc dechlorination of TCE.

Experimental

Unsupported Zinc Powder

Zinc powder was reacted with an aqueous solution of 1000 ppm TCE under a nitrogen atmosphere. The zinc (from J.T. Baker Chemical) was 60 to 200 mesh in size, and was washed in 0.01 M HCl to eliminate any oxide coating. A vacuum tight reaction vessel was charged with 100 ml of nitrogen saturated water and 10 grams of the washed zinc powder were added. A vacuum was drawn on the system and held for 15 minutes to remove any remaining oxygen. The vacuum was broken by introduction of a nitrogen gas stream. The reactor was kept under a constant positive pressure of nitrogen, and 100 μl of TCE was added. High agitation rates were used to insure uniformity of composition. The concentration of chloride ions was measured using a chloride selective electrode.

Supported Zinc

Carbon fiber composite was manufactured using the process described earlier at this conference at CAER, UK. The composite was carbonized at 600 °C to improve the conductivity of the material. A 10 cm long composite sample with 2.54 cm diameter was placed in the holder of the plating apparatus (Figure 1). This sample was immersed in a chloride zinc bath (Table 1) and a plating fluid at 100 ml/min was passed through the sample. A solid zinc electrode was immersed in the bath and an electrode with 2.5 cm diameter was contacted with the carbon composite. A 10 volt, 0.1 ampere current was applied to the composite. This low current density was allowed to flow until a 2 micron layer of zinc was deposited on the composite which had 17 μm diameter fibers.

Scanning electron microscopy and elemental analysis were used to determine the uniformity of zinc coating on the composite support. This composite was then cut and the composite samples used as paddles for agitation in a reactor system as described above in place of the zinc powder.

Results

Zinc Plating

SEM showed that the zinc layer was uniform through out the 10 cm length of the composite and had no radial variation. The zinc layer was 2 μm in thickness. This ease of control of the plating process would allow the composite plating to be regenerated as needed by flowing a zinc-chloride solution through the composite and applying a current as needed *in situ*.

Reaction Rates

To determine if TCE decholorination was occurring, the reaction was monitored for chloride ion concentration in solution using a chloride selective electrode. A typical reaction profile is shown in Figure 2. For this initial study, first order kinetics and total reaction were assumed. Reaction rate constants were determined based on the amount of chloride not released into solution, and are reported on a per gram of zinc basis. The zinc powder was shown to degrade the TCE and the rate of degradation increases with temperature (Table 2).

The reaction rate for the zinc plated composite system is an order of magnitude faster than for the powdered zinc system, indicating that the surface area for reaction of the metal controls the reaction rate. The pressure drop through the zinc plated composite was measured and compared to that of the untreated composite. These values were found to be the same indicating that no increase in pressure drop results from the zinc plating. This pressure drop is low, and the zinc plated composite would be ideal for use in a fixed-bed flow system.

Conclusions

Zero-valent zinc metal has been shown to successfully decholorinate TCE in aqueous solution. The rate of this reaction is determined by the surface area of metal available for reaction. A novel process for depositing zinc metal onto a carbon fiber composite produces a reaction system with high surface area of metal. This zinc plated composite has a reaction rate an order of magnitude higher than that of powdered zinc.

References

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Table 1: Chloride Zinc Bath

$ZnSO_4 \cdot 7H_2O$, g/L	240
zinc, g/L	55
NH_4CL, g/L	15
$Al_2(SO_4)_3 \cdot 18H_2O$, g/L	30

Table 2: First order reaction rate constants for decholorination of TCE by zero-valent zinc.

Type of Zinc	Temperature (°C)	k (min^{-1} g^{-1})
Unsupported Zinc Powder	25	0.000007
Unsupported Zinc Powder	30	0.00001
Unsupported Zinc Powder	40	0.00002
Supported Zinc on Composite	25	0.00025

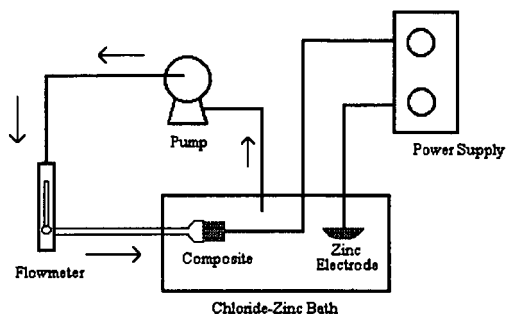Figure 1: Diagram of composite plating apparatus.

Figure 2: Typical reaction profile for powdered zinc degradation of aqueous TCE. Temperature = 40 °C, Initial rate constant, k, = 0.00002 min^{-1} g^{-1}.